

AD-A213 128

MOT-0001AF

Current Injection Pumping of Organic Light Emitters

Prepared by
Jeffrey C. Buchholz
James P. Stec
Mary C. Schutte

DTIC
ELECTE
OCT 04 1989
S D& D

Micro-Optics Technologies, Inc.
8608 University Green #5
Middleton, WI 53562

28 September 1989

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

Contract N00014-88-C-0516

Sponsored by
Strategic Defense Initiative/ Innovative Science and Technology

Prepared for
Office of Naval Research

89 10 2 03 0

Report Title Current Injection Pumping of Organic Light Emitters	Report Date 28 September 1989
Authors Jeffrey C. Buchholz, James P. Stec, Mary C. Schutte	
Performing Organisation Name and Address Micro-Optics Technologies, Inc. 8608 University Green #5 Middleton, WI 53562	Contract Number N00014-88-C-0516
Sponsoring Organisation Name and Address Strategic Defense Initiative/Innovative Science and Technology Office of Naval Research 800 N. Quincy Street Arlington, VA 22217	Type of Report and Period Contractor Report (Final)
Abstract <p>The use of thin films of phthalocyanines as current pumped light emitters was investigated. The growth of phthalocyanine films in a stacked ring crystal structure offers the potential for introduction of electronic structure modulation in the film which could lead to charge carrier confinement and resultant optical emission. Heteroepitaxial stacked ring crystal structures could only be grown to a film thickness of 5 nanometers however. The metal phthalocyanines studied for this growth included copper, magnesium, iron, zinc, fluorochromium, sodium, dichlorosilicon and dilithium. Exposure of ordered films to dopant gases of iodine and bromine affected the crystal structure of the films. The modulated film structures grown did not exhibit fluorescence upon current injection. These films could not be grown in the heteroepitaxial, stacked ring crystal structure which is critical to achieve novel electronic structure modulation. The use of ion beam assist to enhance formation of cofacially joined SiPcO film growth is suggested as a way to enhance heteroepitaxial film growth to greater thickness.</p> <p>These materials are being studied because of their potential as light emitting diodes and laser diodes tunable by chemical means. Devices of these materials are anticipated to have application as integrated optical components. <i>MAJOR 131</i></p>	
Keywords/Descriptors metal-phthalocyanine, organic light emitters, semiconductor device, laser diode, current injection	

Table of Contents

1 Summary	1
1.1 Purpose of the Research	1
1.2 Conclusions	1
2 Introduction	2
2.1 Identification and Significance of the Problem or Opportunity	2
2.1.1 Background, Technical Approach and Anticipated Benefits	2
3 Experimental Procedures	5
3.1 Apparatus	5
3.1.1 Equipment modifications	5
3.2 Procedures	5
3.2.1 Thickness Monitor Testing	5
3.2.2 Deposition from Multiple Source Evaporator	6
3.2.3 Device Structure Design	6
4 Results	8
4.1 Deposition of Layered and Doped Films	8
4.1.1 Layered Composition Film Structure	8
4.1.2 Chemically Doped Film Structure	9
4.1.2.1 Iodine vapor doping	9
4.1.2.2 Bromine vapor doping	12
4.2 In-Situ Fluorescence Characterization of Films	15
4.3 Optical Testing of Device Structures	16
5 Discussion	18
5.1 Chemical Effects on Structure	19
5.2 Current Injection Pumping	19
6 Recommendations	20

Accession No.	
NTIS GRA&I	
DTIC TAB	
Unannounced	
Justified	
by	
per	es

A-1



Table of Figures

Figure 1. Phthalocyanine molecule	4
Figure 2. Energy Level Schematic	4
Figure 3. Stacked ring film growth configuration	8
Figure 4. Surface unit mesh from LEED results	10
Figure 5. Surface unit mesh for iodine on Cu(100) from LEED	11
Figure 6. Model surface unit mesh from LEED results	12
Figure 7. LEED Pattern for Pc/Cu(100) after bromine exposure	13
Figure 8. Surface unit mesh for bromine exposed Pc	14
Figure 9. Cathodoluminescence of Mg-phthalocyanine	16
Figure 10. Cu/340nm.CuPc and MgPc/Al device	17
Figure 11. Predicted space-charge-limited I-V curve	18

1 Summary

1.1 Purpose of the Research

The purpose of this research effort was to explore stacked ring growth of phthalocyanine (Pc) materials for light emitters pumped by current injection.

1.2 Conclusions

We showed that layered metal-phthalocyanine films can be grown with controlled composition and structure by molecular beam epitaxy deposition under ultra-high vacuum conditions.

All of the metal phthalocyanines we have studied, including copper, magnesium, iron, zinc, fluorochromium, sodium, dichlorosilicon and dilithium, grew in the same heteroepitaxial structures on a copper single crystal indicating only a weak interaction of the central metal atom with the substrate.

Multilayer structures with alternating monolayers of different metal phthalocyanines have also been grown without apparent degradation of film structure indicating that layered structures can also be successfully grown.

While the phthalocyanines grew in a structure consistent with a stacked ring type structure near the copper crystal growth interface, the film apparently loses its stacked ring nature by approximately 5 nm film thickness.

Films were exposed to several dopant gases during deposition to try to increase stability of the epitaxial type of film growth to allow greater film thickness in the stacked ring structure. Exposure to large doses of oxygen and methylene chloride had no effect on film growth. Exposure to iodine vapors caused the film to cease having the planar phthalocyanine molecule parallel to the substrate surface on initial deposition.

Exposure of ordered films to bromine vapors resulted in a larger unit cell than for pure phthalocyanine. This suggests a model with the phthalocyanine still aligned parallel to the substrate but incorporating bromine.

Crystal structure control within the film is critical in achieving novel materials structures for device applications. The stacked ring structure initiated by epitaxy with the substrate did not persist to film thicknesses suitable for devices for pure phthalocyanines. This structure was not stabilized by introducing the molecular dopants used in this study. Stabilization of this epitaxial growth through ion assisted deposition to achieve cofacially joined materials remains a possible way of achieving this that was not fully studied in this Phase I effort. It may provide a means of keeping the molecular film from evolving into its non-stacked ring equilibrium crystal structure. That work remains for future studies.

Devices of a metal/phthalocyanine/metal structure have been tested for fluorescence by current injection but did not show fluorescence. Electrical characteristics of these devices are typical of space charge-limited (SCLC) conduction in an organic semiconductor. Because of the present limit on the film thickness in maintaining a stacked ring structure, these current injection pumping experiments have largely been on films without epitaxial structure throughout the film.

Cathodoluminescence studies have shown strong electron beam excited fluorescence at about 520 nm from multilayer films including magnesium-phthalocyanine. This is attributed to magnesium fluorescence since it is also observed for pure magnesium-phthalocyanine films but not for other phthalocyanines.

2 Introduction

The object of this research effort was to explore phthalocyanine based organic semiconductor materials as light emitters pumped by current injection.

This work was motivated by previous observations that phthalocyanine films grown under ultrahigh vacuum conditions on clean single crystal substrates appear to grow in a crystal structure similar to the stacked ring structure that can be grown for bulk materials. This heteroepitaxial growth mode for thin films allows the potential for the introduction of electronic structure modulation in the film which could lead to charge carrier confinement and resulting optical emission.

This modulation of properties was studied using material substitutions, gas phase doping and intermolecular chemical bonding.

This work consisted of two major tasks:

1. Characterization of structural modification of film growth when modulation is introduced into the film composition.
2. Fabrication of test devices for studies of optical emission excited by current injection for the materials produced under Task 1.

2.1 Identification and Significance of the Problem or Opportunity

We have previously studied laser induced fluorescence from thin films of Zn-Phthalocyanine and Mg-Phthalocyanine under a 1985 NSF-SBIR Phase I grant. Emission was seen as broad bands extending from about 800nm to 1100nm and 700nm to 1100nm respectively. Fluorescence was excited with a HeNe laser.

We observed that the emission from Mg-phthalocyanine is peaked near the absorption band due to the π - π^* singlet excitation. There is a tail to lower photon energy extending to 1100nm which we feel may be due to phonon excitation.

The emission from Zn-phthalocyanine is peaked in a band removed from the π - π^* primary excitation in what is thought to be an exciton band around 900nm. The intensity within this band could be shifted in wavelength by varying deposition conditions including introduction of bromine containing 'dopant' impurities.

These results showed the emission spectrum of thin films of phthalocyanines to be sensitive to deposition parameters resulting in either incorporation of 'dopant' impurities or changes in film crystal structure.

2.1.1 Background, Technical Approach and Anticipated Benefits

The phthalocyanines have been previously studied for light emission properties primarily in solution^[1]. Those that have appreciable solubility in an acceptable solvent, and that is only a few special cases, have been studied for stimulated emission^[2] and as saturable absorbers^[3]. Because of the high thermal stability of these materials they have also been studied in the vapor phase^[4], as vapor transport grown single crystals^[5] and as vacuum deposited films^[6]. The motivation for much of this work was to explain the energy transfer processes within these large molecules following excitation.

In recent years there have been developments of novel materials based on the phthalocyanines grown in what is referred to as a 'stacked ring' structure. These materials, grown by chemical means, usually have the Pc molecules stacked with the planar molecules face to face^[7]. This structure is usually, but not always^[8], grown with

chains of halogens, principally iodine^[9] arranged between the phthalocyanine stacks. The resultant materials have electrical properties much different than the pure phthalocyanine material and often exhibiting reduced dimensionality because of the highly anisotropic structure presented by the largely one-dimensional stacking of the phthalocyanine rings with coupling much stronger along the stacks than between the stacks^[10]. The electrical property variations can be so large that these materials are sometimes referred to as 'molecular metals'.

The change in conductance of reduced or oxidized phthalocyanine films has been demonstrated for a metal/phthalocyanine/metal structure^{[11][12]}.

In our own earlier work with thin films of phthalocyanines deposited on clean, well ordered, and chemically selected substrates^[13] under ultra-high vacuum conditions, we grew films with a structure consisting of the planar phthalocyanine molecules stacked parallel to the single crystal substrate in an epitaxial manner. This structure is similar to the stacked ring structure of the chemically grown 'stacked ring' and 'cofacially joined' materials showing novel electrical properties^[14].

The structure we observed in that work was different from that reported by previous workers on thin film structures reported as epitaxial^[15] by our use of ultra-high vacuum conditions and our choice of an atomically clean substrate which satisfies conditions of 'lattice matching' for such a heteroepitaxial situation. Their choice of a substrate with strong directional bonding probably leads to the crystal structure they observe which is the normal bulk structure. The substrate we used successfully was a Cu(100) single crystal surface. This surface has a lattice constant which allows a planar molecule of the dimension of the phthalocyanine to pack in registry with the substrate in a large two-dimensional superlattice structure. Copper was also found suitable because the weak chemical bonding of copper for aromatic hydrocarbons does not tie the deposited molecule so tightly to the substrate crystal structure that accommodation to molecular packing constraints cannot take place. This planar structure was not observed by us for substrates that did not meet these conditions. Growth in this structure has been verified by others working with this substrate under ultra-high vacuum conditions^[16]. Because of the similarity of this thin film structure with the chemically grown 'stacked ring' structures, we intend in this effort to see if this combination of thin film epitaxy and chemical modification of properties can be used to modify the optical fluorescence of these materials for use as thin film light emitters.

The phthalocyanine (Pc) molecule is as shown in Fig.1. The central metal position in this planar molecule can be occupied by essentially any metallic element or the molecule can be metal-free, H₂Pc. The largely similar optical absorption spectrum and fluorescence spectrum, where it has been observed, of the metal and metal free phthalocyanines suggest that the optical response is predominantly from the conjugated organic system of the organic ring modified by the central metal atom or chemical modifications to the ring itself. Solution and vapor phase work^{[17],[18]} give largely a measurement of the isolated molecular properties although absorption and fluorescence properties show a dependence on solvent or supporting matrix^[19].

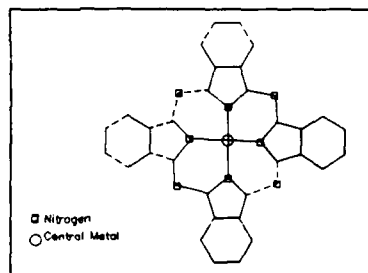


Fig. 1. Phthalocyanine molecule

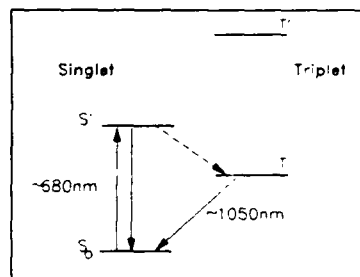


Fig. 2. Energy level schematic

The energy level diagram for the phthalocyanine molecule, in solution or in the vapor phase, is qualitatively shown in Fig.2. For essentially all phthalocyanines, the optical absorption peaks around 680nm which is approximately the first excited singlet S_1 to ground state singlet S_0 separation^[20]. The triplet state T_1 can become significantly populated and result in quenching of S_1 - S_0 fluorescence and radiative decay of the long lived triplet state resulting in phosphorescence. This phosphorescence has been observed at low temperature^[21] and results in sharp line emission at around 1150nm. This phosphorescence is reported to decrease with increasing temperature however. No emission in this energy range was seen in our previous room temperature experiments. This intersystem crossing to the triplet state increases for paramagnetic central metal atoms and increases with the atomic number of the central metal atom through increased spin- orbit coupling^{[22],[23]}. In our work we studied primarily light metal phthalocyanines to minimize this intersystem crossing. In solid state materials, either single phthalocyanines crystals or thin films, fluorescence has previously been observed between approximately 800nm and 1100nm. This fluorescence removed from the π - π^* singlet excitation has been ascribed to exciton formation^[24]. This is the region of the emission spectrum we intend to study in this work. It is the most likely to be readily modified by chemical modification of thin film structures. There has also been observation of higher energy fluorescence in the visible reported^[25]. This spectral region was not investigated in our own work because the HeNe laser excitation source used for those studies limited the energy range to less than 632.8nm.

In addition to providing materials engineering by chemical modification of the starting molecular species or doping from the gas phase during film growth, we intended to show control of properties by growth of artificial structures using what is essentially our molecular beam epitaxy approach. This approach was used to grow film structures that incorporate film property modulation to enhance both the optical emission properties of the materials and electronic properties to provide and enhance current injection pumping of the optical emission. In general terms we will pursue this objective of injection pumping of the structures by alternating layers of 'molecular metal' doped material with materials which have exciton type emission states, as in ZnPc, to form confined exciton wells^[26].

3 Experimental Procedures

3.1 Apparatus

3.1.1 Equipment modifications

Early results of Low Energy Electron Diffraction (LEED) studies of Cu phthalocyanine deposited on clean Cu(100) crystals showed the structure of the deposited film starting at monolayer quantities to be sensitive to the deposition rate of the film. Ordered heteroepitaxial growth into the stacked ring structure appears to take place only at very low deposition rates.

These observations are for room temperature substrates. We suggest that this is likely due to competition between surface mobility and the arrival rate of the condensing molecules. For high arrival rate only a disordered film structure is observed in LEED. Because LEED does not readily distinguish between an amorphous structure or a polycrystalline film we cannot unambiguously determine the structure of the film from the current experiments. We believe that this structure is probably a polycrystalline film with crystallites of the equilibrium crystal forms of phthalocyanine that have been observed by others for sublimed films.

In our present experimental apparatus, film deposition rate is determined using a commercial quartz crystal thin film rate monitor. This does not provide particularly accurate results for the low rates necessary for heteroepitaxial film growth on a room temperature substrate. There is always a desorption rate from the quartz crystal maintained at room temperature that causes a decay of the observed total deposited thickness at a rate of about 0.2nm/min. This desorption rate appears to be of the same order as the deposition rate which produces heteroepitaxial growth.

3.2 Procedures

3.2.1 Thickness Monitor Testing

As a further approach to film rate and in-situ film thickness measurement we investigated the limit of thickness that could be measured based on the optical absorption of the film by measurement of transmission through the film deposited on a transparent substrate.

This approach to deposition rate control was used because both conventional quartz rate monitor measurements and direct measurement of absorbed power in the deposited film were previously shown to be inadequate for providing real time control of deposition rate which appears important for growing the film in the desired crystal structure.

Because phthalocyanine is a relatively strongly absorbing material at the He-Ne wavelengths used in our measurements with an absorption coefficient of about $2 \times 10^5 \text{cm}^{-1}$ we were able to detect film thickness changes of order 3nm with this approach. This approach was found to only be useful in providing a calibration of the sublimation source operating conditions.

It was not found to be possible to provide a practical way of maintaining the actual deposition substrate in a stable and reproducible position in the sample positioner in the vacuum chamber while maintaining the precision needed to adequately determine rate from the absorption measurement.

Absorption measurements on test specimens provided a good calibration of rate with operating conditions for the new source design described in the following section. Film thickness will be estimated by source operating conditions rather than by any method of real-time deposition rate determination.

3.2.2 Deposition from Multiple Source Evaporator

Previous evaporator designs have all relied on heating the evaporation charge by radiation from an incandescent filament surrounding the charge. This made actual sublimation temperature difficult to determine and control because temperature could only be measured with a thermocouple also radiatively heated. The recorded sublimation temperature was thus very sensitive to source geometry and reproducible deposition rates from run to run were nearly impossible to the accuracy desired.

A new sublimation source consisting of a heated quartz or alumina surface in contact with a copper evaporation oven was constructed and tested. The metallic copper baffle provided an improved way of providing uniform source temperature and a stable and readily measured sublimation temperature. To overcome the poor heat transfer by powdered phthalocyanine used in earlier attempts with non-radiatively heated sources, the phthalocyanine was loaded as a painted on paste or an evaporated film on the walls of the alumina surface and copper baffles.

Pasting of the phthalocyanine used a slurry of the phthalocyanine in acetone or methanol. The solvent evaporated relatively rapidly leaving a pasted on thick film on the sublimation source. No acetone or methanol was seen in the vapor phase after the system was baked and evacuated to UHV pressures.

There was, however, a relatively large increase in CO_2 (mass 44) partial pressure whenever the sublimation source was initially heated.

A LEED pattern indexed as $(2\sqrt{2} \times 2\sqrt{2})R45$

was observed on heating of the sublimation source to temperatures less than those usually required for phthalocyanine deposition. This is also the range of temperature that gives a significant rise in CO_2 in the background gas. The remaining peaks in the mass spectrum to the measurement limit of mass 100 look like those seen during deposition of phthalocyanine though this mass range covers only the indole group and smaller fragments. This LEED pattern is not seen when the clean copper is exposed to CO_2 leaked into the chamber or if the copper is not in line of sight of the sublimation source.

The unit mesh dimension of the $(2\sqrt{2} \times 2\sqrt{2})R45$

structure is only 0.72nm compared to the phthalocyanine molecular dimension of about 1.37nm. Thus we conclude that this pattern is likely due to a fragment of the phthalocyanine molecule caused by preparation with acetone or methanol.

Because of this increased 'dirt' for initial deposition from these samples, we have determined that the best way to prepare clean, reproducible films is to start with phthalocyanine evaporated into our sublimation sources from the commercial powder.

3.2.3 Device Structure Design

Discrete device structures of modulated phthalocyanine films between metal contacts were grown under UHV conditions. The active area of each device is approximately $6 \times 10^{-4} \text{ cm}^2$.

These devices were fabricated on three inch silicon wafers using shadow masks in a multistep process. The bottom contact material, 500nm thick, was deposited on clean polished single crystal (100) silicon in stripes 3.0mm wide spaced 3.0mm apart. This material was either sputtered copper or thermally evaporated gold or titanium. A 250nm thick magnesium fluoride film was deposited over the 3.0mm bare silicon stripes and just overlapping the metal stripes. These depositions took place in a turbo-pumped bell jar, base pressure 1×10^{-7} torr, equipped for RF and DC sputtering, electron beam deposition and thermal evaporation.

The silicon wafer was then removed from vacuum and cleaved along the middle of the copper stripes and perpendicular to the stripes to form rectangles approximately 6mm wide and 20mm long. A cleaved piece was inserted into the UHV chamber which was evacuated and baked to a base pressure better than 1×10^{-9} torr. The piece was sputtered in an Argon atmosphere for one hour. This was immediately followed by a sequential deposition of two different types of phthalocyanine in 1nm layers from the multiple source evaporator described above. The total thickness of phthalocyanine deposited was varied for each sample. For the final step a mask with several open stripes .4mm wide was then brought into position over the sample so that these stripes were perpendicular to the copper stripes. Several hundred nanometers of either aluminum, copper or gold were then deposited onto the device. This process yielded several discrete devices on each rectangle. A device consisted of a metal bottom electrode, a modulated phthalocyanine film and a metal top electrode of area approximately $6 \times 10^{-4} \text{ cm}^2$ with an exposed phthalocyanine edge.

Devices were constructed with copper and magnesium phthalocyanine modulated films with total thickness of 100, 140, 240 and 250nm or with magnesium and zinc phthalocyanine modulated films 340, 430, 516, 600, 1000 and 1170nm thick.

4 Results

4.1 Deposition of Layered and Doped Films

A movable shutter is placed in front of the multiple evaporation sources to provide a sequence of deposited materials.

Preparation of reproducible multilayer film structures was hampered by unavailability of a sufficiently sensitive real time monitor for phthalocyanine deposition rate to enable active control of the multilayer film growth sequence. We have had to rely on sublimation source calibrations for control of film growth.

4.1.1 Layered Composition Film Structure

The structure of sequentially deposited films with substituted central metal atoms has been characterized by Low Energy Electron Diffraction (LEED). This measurement determined if the central metal atom in the phthalocyanine affected the growth of the film in a planar stacked ring growth mode on a Cu(100) single crystal surface.

Tested were copper, magnesium, iron, zinc, fluorochromium, sodium, dichlorosilicon and dilithium phthalocyanines. All of these materials began growing on a clean Cu(100) surface in the structure previously described as consistent with the molecule laying flat on the surface as determined by the size of the surface unit cell determined from the diffraction pattern.

After the initial epitaxy, the type of phthalocyanine was changed by changing the shutter selection and deposition was continued. The deposition was then continued until pattern quality deteriorated with increasing film thickness.

In all cases tested, the nature of the central metal atom in the phthalocyanine had no appreciable effect on the structure formed in either the initial monolayer structure or in the surface structure observed from the thicker films. At least on a relatively weak bonding substrate like copper, the central metal atom in phthalocyanine has little effect on initial bonding or subsequent film growth.

There was some difference in the quality of the patterns observed for different materials. This may, however, be due to the relative purity and stability of the various materials rather than the direct influence of the metal type on bonding.

A model of the arrangement of phthalocyanine stacked in a surface unit cell of the size determined by LEED studies of the various phthalocyanines is shown in Fig. 3.

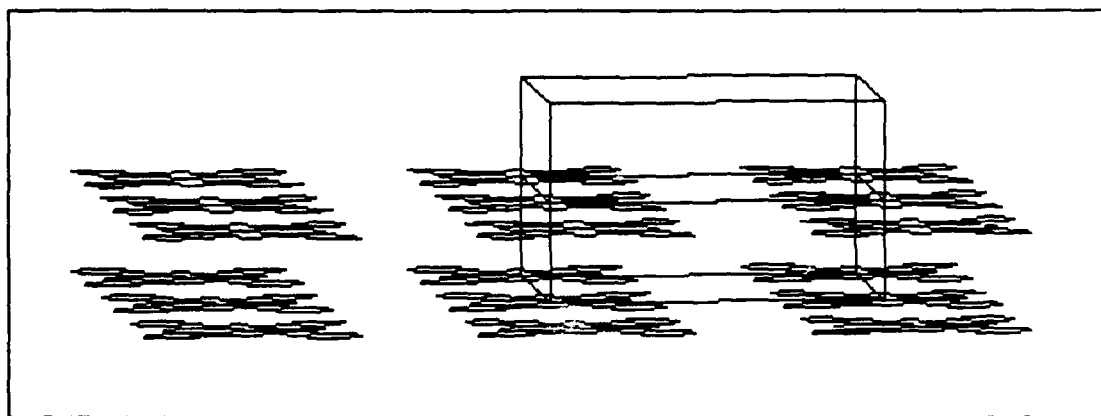


Figure 3. Stacked ring film growth configuration

4.1.2 Chemically Doped Film Structure

Film structure was studied by LEED for films exposed to doping vapors. Materials studied as dopants were oxygen, iodine, bromine and methylene chloride.

Doping exposures were generally begun after at least an initial ordered layer of phthalocyanine was deposited on the clean copper. An initial ordered layer of iodine was also used as the substrate for subsequent film growth. The deposited ordered film of phthalocyanine was either exposed to the vapor after film growth was stopped or during film growth.

Film growth during doping vapor exposure did not yield ordered film growth for any of the materials combinations tested.

Subsequent exposure of phthalocyanines to oxygen or methylene chloride vapors did not yield any changes in the ordered structure of the films until very large exposure doses or pressures. Under these conditions loss of surface order was generally observed. Because of the high exposures to the vapor it is difficult to determine if the loss of order was due to incorporation of the vapor into the film or if adsorption of contaminants from the vapor resulted in a contaminated film surface.

For the exposures to iodine and bromine there were changes in the surface structure deduced from the LEED patterns that can be interpreted as changes in the structure of the films.

4.1.2.1 Iodine vapor doping

As reported earlier, the LEED pattern observed for ordered phthalocyanine films of thickness to five or ten molecular layers is consistent for a model of the surface as shown in the figure.

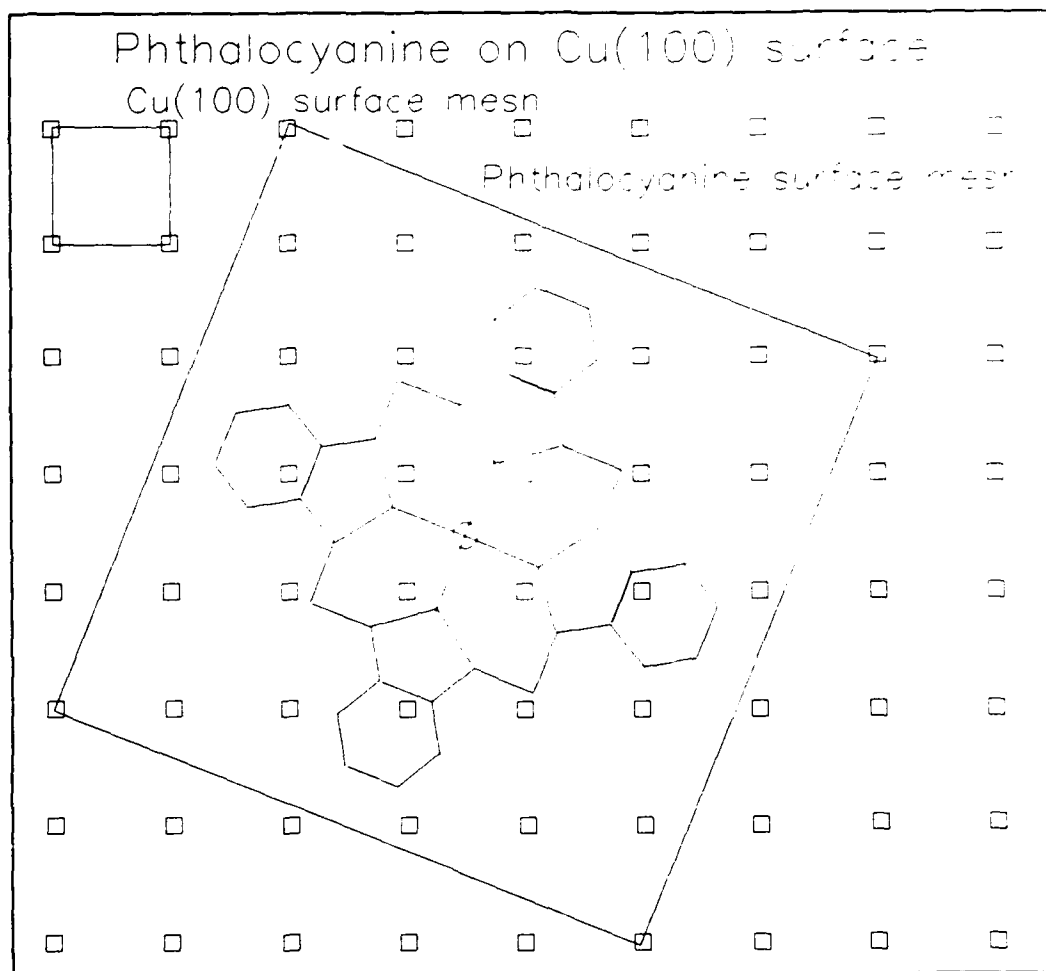


Figure 4. Surface unit mesh from LEED results

On iodine exposure and heating of the copper crystal, the pattern evolves through various complex intermediate stages to a pattern with a surface symmetry referenced to the clean copper surface cell of $c(6 \times 4)$. The size of this surface unit cell is no longer large enough to accommodate the phthalocyanine molecule in a flat configuration parallel to the copper surface. We conclude that the molecule is being shifted toward an on-edge configuration.

The $c(6 \times 4)$ surface cell is similar to the surface structures observed for iodine adsorbed on clean Cu(100). Iodine initially adsorbs on Cu(100) in a $c(2 \times 2)$ structure but on slightly further exposure changes to a $c(6 \times 2)$ structure. There need be no significant change in surface coverage between these structures. It is likely that the $c(6 \times 2)$ structure results from only a small out of plane or lateral shift of some rows of atoms.

Models of atomic iodine adsorbed on Cu(100) that are consistent with the LEED results are shown in Fig. 5.

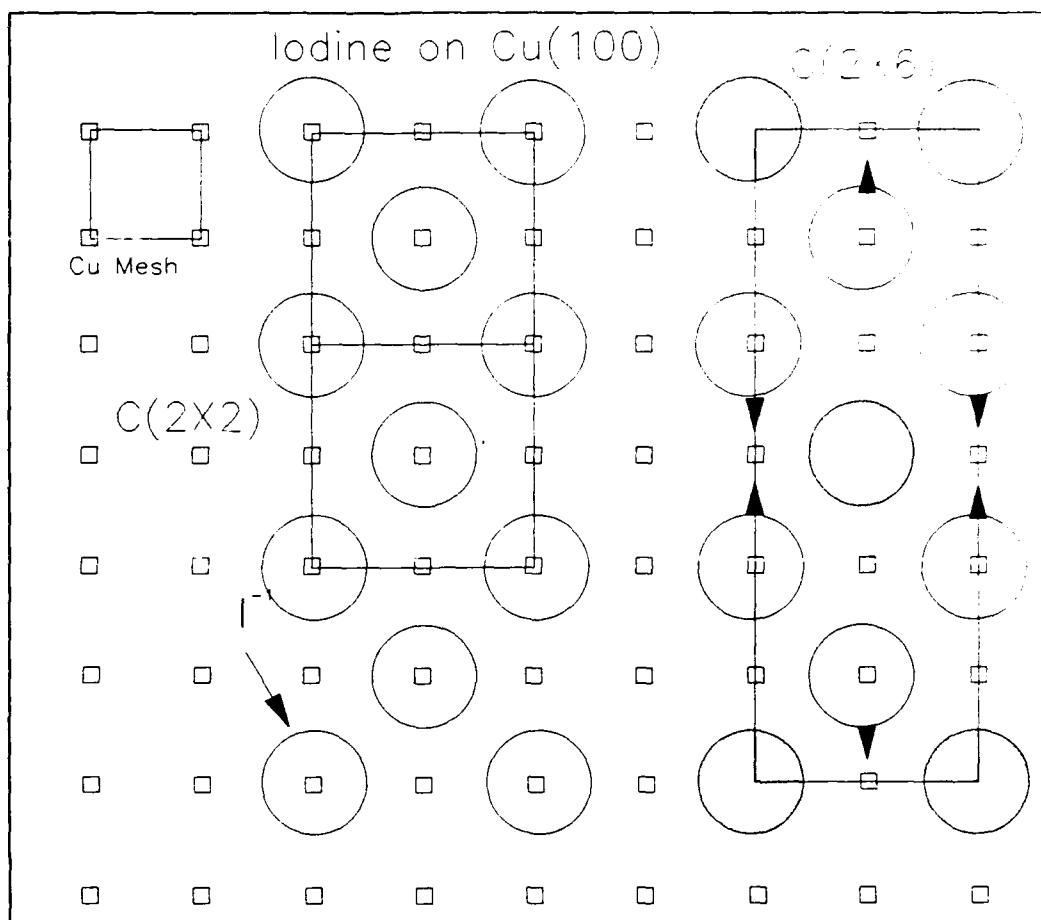


Figure 5. Surface unit mesh for iodine on Cu(100) from LEED

The $c(6 \times 4)$ structure observed for phthalocyanine following iodine doping and heat treatment can be formed by a union of two (2×6) cells with further distorting of phthalocyanine positions to decrease the surface symmetry.

A model of a surface structure consistent with this result is shown in the figure. The iodine is placed at positions corresponding to full coverage. On further heating of this structure the LEED pattern returns to the $c(6 \times 2)$ structure observed for iodine exposure of clean copper alone. This occurs at a much lower temperature than is required for removal of phthalocyanine from the surface without iodine exposure.

We conclude that the strong bonding of iodine to copper dominates the film structure. The phthalocyanine has been displaced from its optimized bonding to copper, a flat configuration to maximize van der Waals bonding. The surface structure formed is thus similar to that formed by iodine on copper where the interaction with the phthalocyanine and the phthalocyanine molecular size do not cause steric hindrance.

A model structure with the $c(6 \times 4)$ symmetry illustrating the possibility of incorporating a molecule the size of phthalocyanine standing on end is shown in the figure.

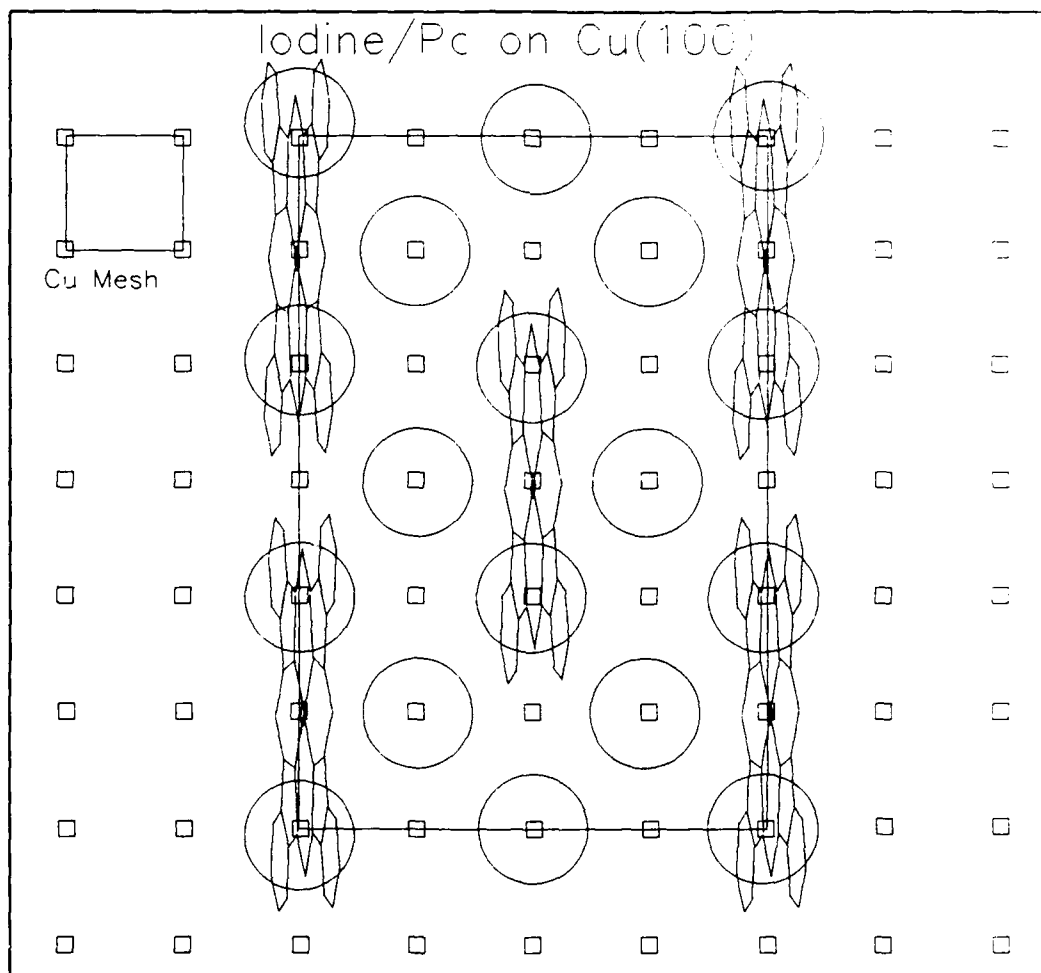


Figure 6. Model surface unit mesh from LEED results

4.1.2.2 Bromine vapor doping

Substitution of bromine for iodine leads to entirely different behavior. The LEED pattern observed after bromine exposure of phthalocyanine on Cu(100) is shown schematically in Fig. 7 below.

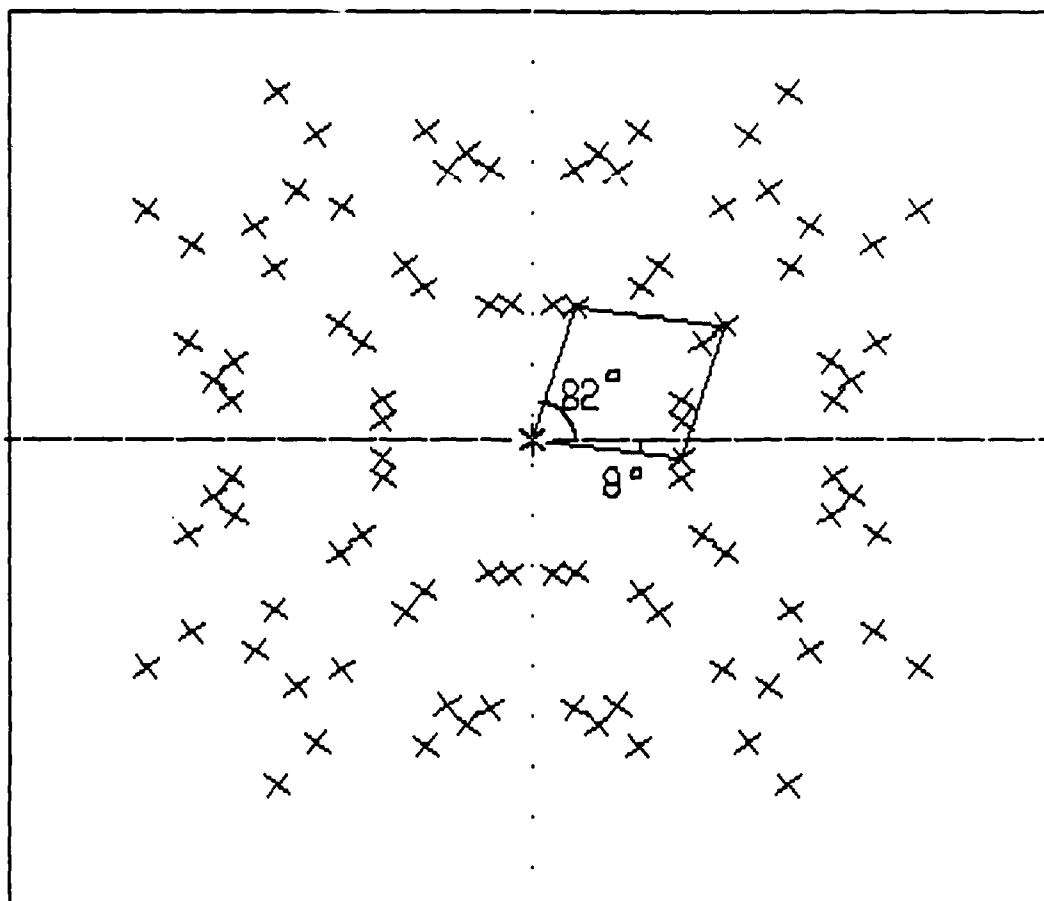


Figure 7. LEED Pattern for Pc/Cu(100) after bromine exposure

The unit mesh dimension of this new structure is about 1.80nm in a non-square cell. Pure phthalocyanine has a square cell with dimension of 1.37nm. The unit cell after bromine exposure remains in registry with the underlying copper substrate but the cell size, shape and orientation are changed. The surface cell for the Pc/Bromine structure is compared to that for pure Pc in Fig. 8 below. The pure Pc cell and molecule are shown in an arbitrary position and orientation only for size comparison. There is not information available from the diffraction results to actually locate the molecule.

Pc/Bromine on Cu(100)

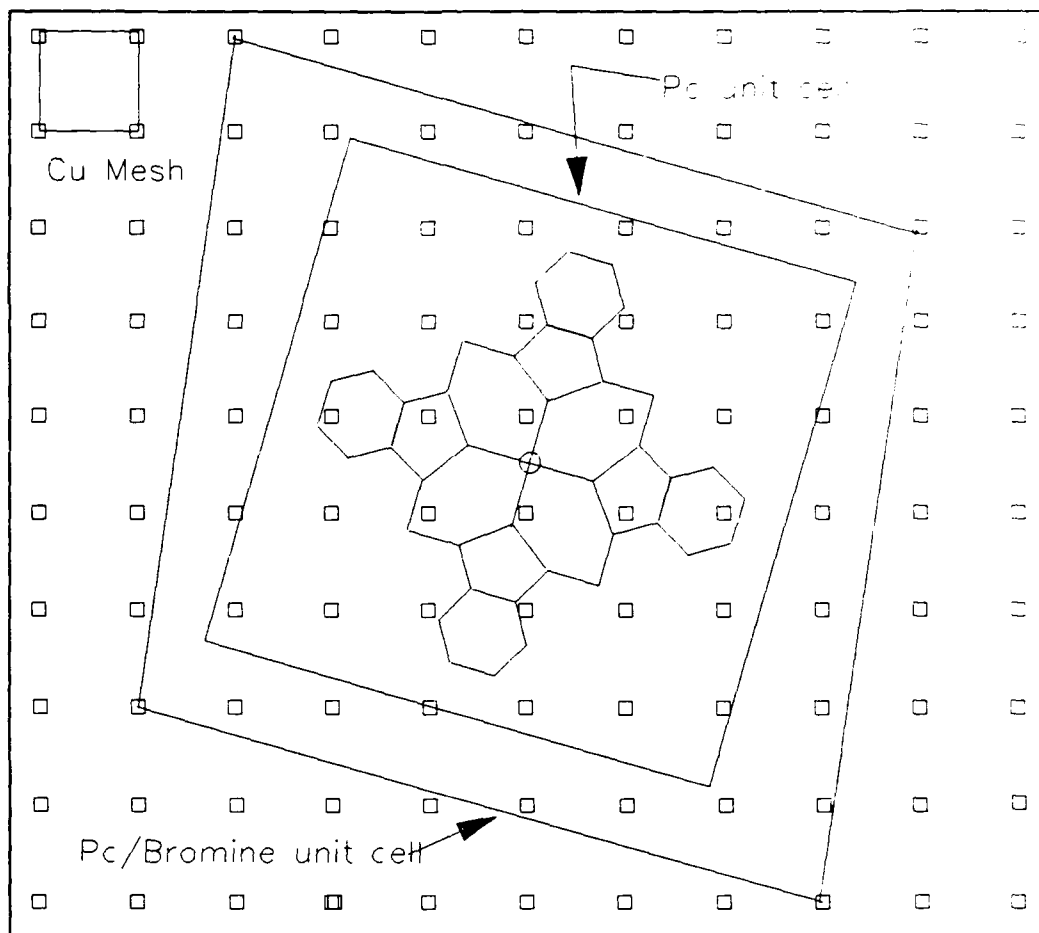


Figure 8. Surface unit mesh for bromine exposed Pc

Heating of the doped film results in apparent removal of the phthalocyanine with the $c(6 \times 2)$ bromine on copper(100) pattern remaining.

These results indicate that, unlike the case of iodine exposure where the iodine/substrate interactions apparently dominate resulting in a unit cell size that can only be accounted for with the phthalocyanine standing up, the unit cell for bromine exposure is large enough to accommodate the Pc molecule, parallel to the surface, and bromine incorporated into the cell. The Pc/bromine unit cell is 72% larger in area than the cell for pure Pc. Because LEED cannot locate the molecules within the cell, it is possible that there is more than one molecule per cell, inclined to the copper surface. The thermal desorption of the phthalocyanine resulting in a clean surface, observed after bromine and iodine exposure, indicated a weakening of the

phthalocyanine bonding to the copper from that of the pure phthalocyanines believed parallel to the surface. The pure phthalocyanines could not be desorbed without decomposition of at least the first layer to a carbonaceous residue.

Since the pattern becomes a $c(6 \times 2)$ bromine pattern after the phthalocyanine desorbs, we can place limits on the amount of bromine in the cell. If the bromine completely covered the copper surface in the $c(6 \times 2)$ structure indicated in Fig. 5, there must be eight bromine atoms in the surface unit mesh shown in Fig. 8. This is an upper limit since a good deal of the surface could be bare copper after the phthalocyanine desorption and the LEED pattern observed would arise from islands of bromine on the copper. LEED is unable to distinguish between these cases.

4.2 In-Situ Fluorescence Characterization of Films

We have been monitoring film properties after growth by both photoluminescence and cathodoluminescence. Photoluminescence was excited with a HeNe laser as was done in our previous work^[27] on single component phthalocyanine films. Cathodoluminescence was excited by the RHEED electron gun operating at approximately 2.0 microamp beam current at a beam energy from 1-10 keV.

The luminescence was filtered by a monochromator and measured by a photomultiplier with an extended S5/UV response.

The most readily observable fluorescence was observed for Mg-phthalocyanine and multilayer structures incorporating Mg-phthalocyanine. Photoluminescence using He-Ne laser excitation was observed in a broad peak between 700-800 nm.

A strong cathodoluminescence in the visible was observed from freshly deposited Mg-phthalocyanine. It was sensitive to electron beam exposure, decaying quickly under beam exposure. The fluorescence was much less sensitive to beam effects when the film was a multilayer film of Mg- and Cu-phthalocyanine deposited with a periodicity of 10 nm. Visual inspection of the film shows no material loss in the irradiated region but suggests changes in film morphology and thus possibly crystal structure in the electron beam irradiated region.

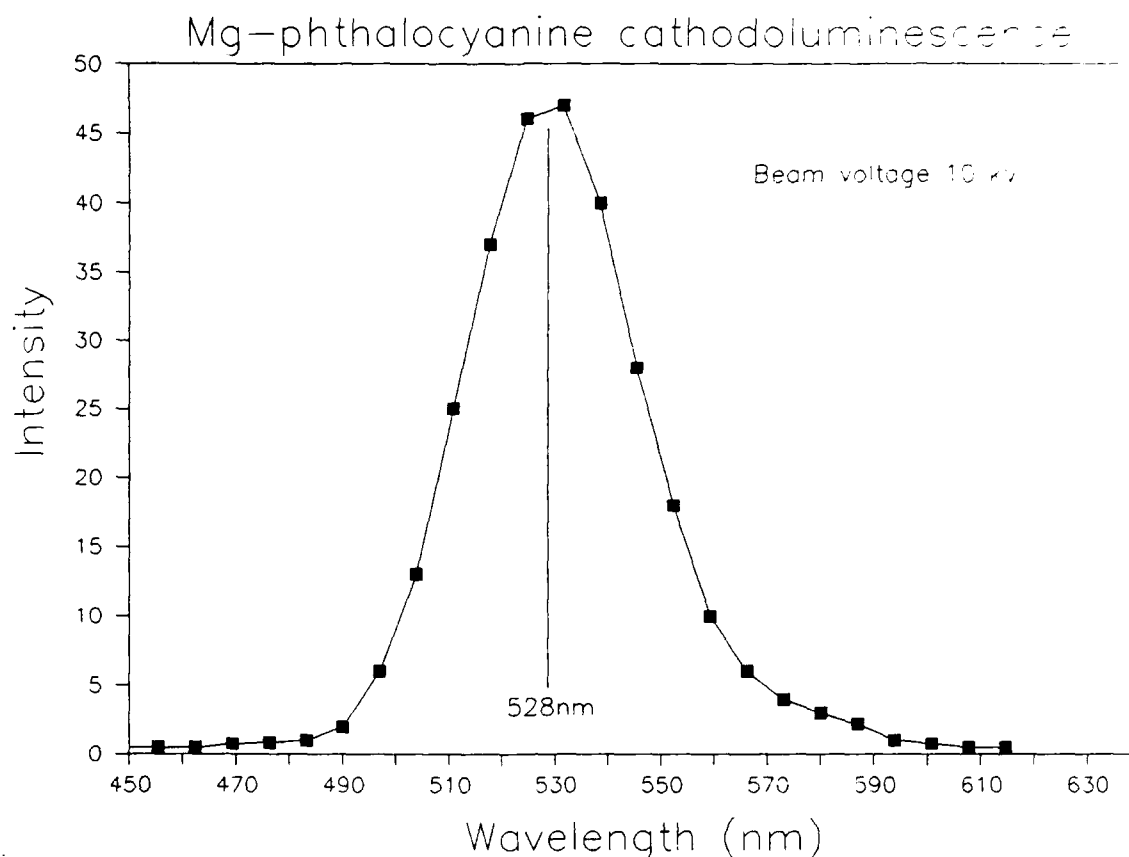


Figure 9. Cathodoluminescence of Mg-phthalocyanine

The single peak in the cathodoluminescence spectrum at about 528 nm is shown in the figure. The time response of this fluorescence and film structure dependence of the fluorescence to determine its origin and usefulness in device fabrication should be studied.

4.3 Optical Testing of Device Structures

After fabrication, the samples were placed in a light tight box for emission studies and to eliminate the possibility of photoelectric effects which have been reported in phthalocyanines^[28]. Contact to the top and bottom contacts was made by gold tipped spring loaded electrodes. Current injection to the samples was from a precision current source with a DC-100 kHz analog voltage control/modulation port. Voltage across the device was measured by an A/D with 13 bit resolution. During testing, current to the device was ramped from 0 to a maximum of 200ma. Imposed on this ramp was a modulation that could be varied from 0 to 30ma in amplitude at a frequency of 0.5 to 500 Hz.

Both a photomultiplier tube and a Lead Sulfide photoconductor were used to measure any emission from the device. This gave a spectral range of approximately 0.2 to 3.4 microns that could be detected. The photomultiplier tube had extended SS/UV response. The photoconductor had a responsivity of 6.0×10^4 VW⁻¹. They were positioned to collect from the edge of the device. When a modulation was imposed on the current to the sample the

outputs of the PMT and the photoconductor were measured by a lock-in amplifier. If there was no modulation of the current the outputs of the detectors were sent through a preamplifier to a ratemeter.

Devices where the thickness of the modulated phthalocyanine film was on the order of 100nm or less gave current vs voltage (I-V) curves indicating ohmic conduction and had resistance values equal to that of the metal contacts with no intermediate film. This is due to pinholes in the phthalocyanine films giving conduction dominated by metal to metal contacts.

Devices with phthalocyanine films 140nm or thicker always showed some indication of space charged limited conduction (SCLC) as seen by Sussmann^[29] and Gould^[30]. A typical I-V curve from one of the devices tested is shown in Fig. 10. This device had a copper bottom electrode, a 340nm thick CuPc and MgPc modulated film and an Al top contact. Figure 11 shows the predicted, from Gould, space-charge-limited I-V curve for a metal-340nm CuPc-metal film of area $6 \times 10^{-4} \text{cm}^2$. Differences in the voltage values could be attributed to the deposited film being thicker than 340nm.

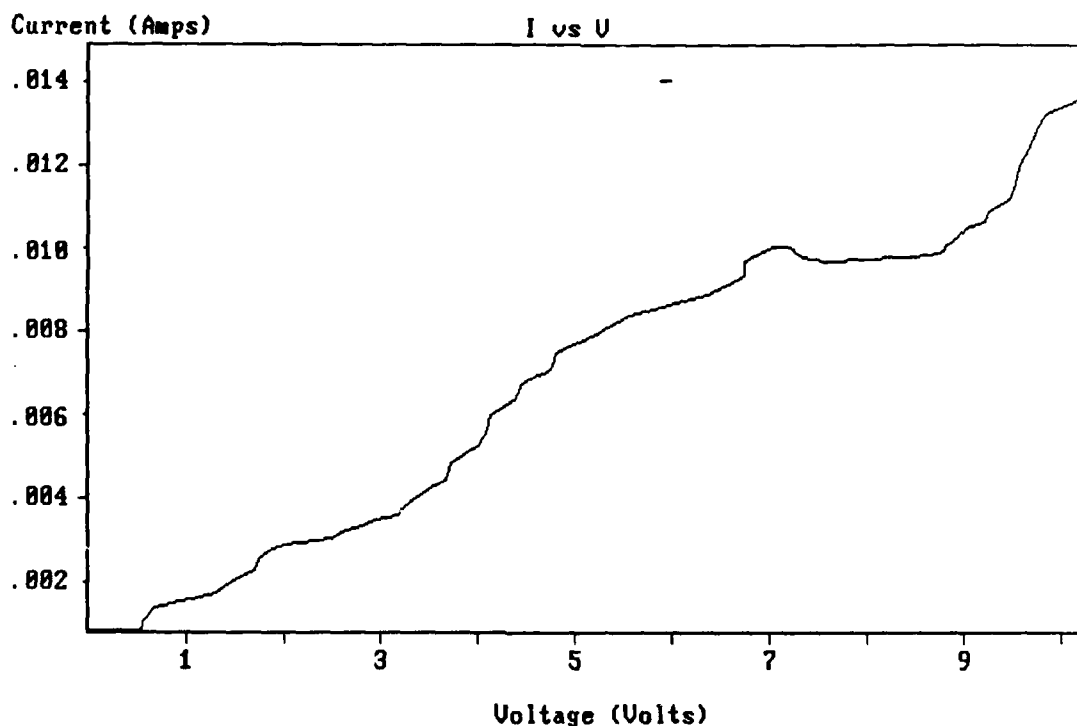


Figure 10. Cu/340nm.CuPc and MgPc/Al device

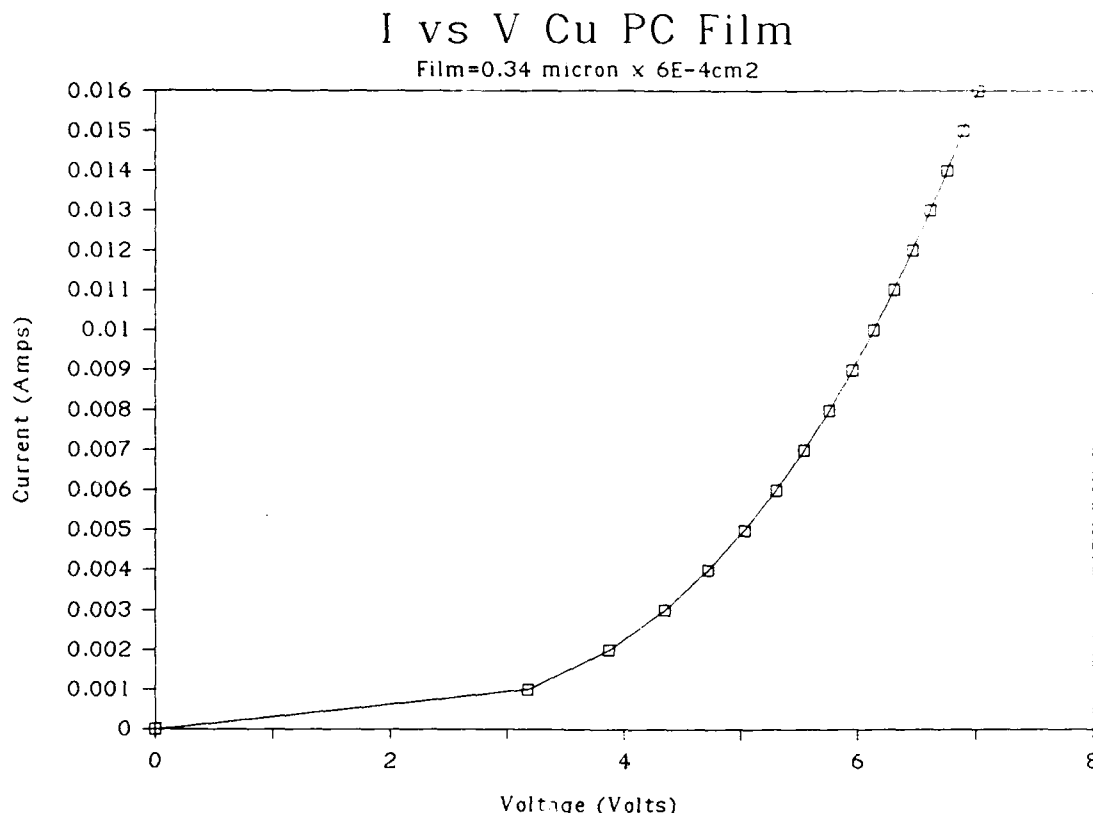


Figure 11. Predicted space-charge-limited I-V curve

Some devices went from SCLC to ohmic conduction as higher currents were injected. In these cases the power density must have been sufficient that some areas of the Pc film had evaporated or flowed resulting in a metal to metal contact.

No emission in the detectable range, 0.2 to 3.4 microns, was measured from any of the samples during current injection. This was true for current injection with a large modulation, 30ma amplitude at 500Hz, imposed on the ramp as well as for a straight DC ramp of the current.

5 Discussion

This work investigated the feasibility of using thin films of organic semiconductors as current pumped light emitters for light emitting diode and laser diode applications. We showed that layered metal-phthalocyanine films can be grown with controlled composition and structure by molecular beam epitaxy deposition under ultra-high vacuum conditions. The control provided by this approach provides a means of growing films with a modulation of materials properties throughout the film that is not available in films grown under less controlled conditions.

We combined film growth under ultra-high vacuum conditions with use of atomically clean Cu(100) single crystal substrate and film characterization during growth by Low Energy Electron Diffraction and Auger spectroscopy to determine the molecular ordering in these organic semiconductor films.

5.1 Chemical Effects on Structure

We monitored the role of varying the central metal atom of the phthalocyanine during growth on any resultant change in film growth morphology. All of the phthalocyanines studied grew in the same initial planar heteroepitaxial structure on the Cu(100) substrate. This indicates a weak interaction of the central metal atom with the substrate. Varying the central atom within the deposited film also has no effect on film structure. This allowed growth of multilayer structures with alternating monolayers of different metal phthalocyanines.

Ordered planar growth of the phthalocyanine molecules as determined by LEED could only be observed for films less than 5nm thick. Beyond that thickness, LEED showed the presence of a disordered or polycrystalline film. These cases cannot be distinguished because LEED requires a single crystal surface. Our measurements of film structure by reflection high-energy electron diffraction (RHEED) were not successful.

The effect of exposure to doping gases on film structure was also studied by LEED. Dopant gases studied were oxygen, methylene chloride, iodine and bromine. Vapor exposure during film growth did not yield ordered films for any of the material combinations tested. This suggests that the interaction of the phthalocyanine molecule with the copper substrate is easily disturbed by the arrival of a competing molecule.

Exposure of oxygen or methylene chloride to an ordered phthalocyanine film showed no effect until very large exposures. This loss of order could be due to incorporation of the vapor into the film or more likely by the adsorption of contaminants from the vapor on the copper.

Exposure of ordered Pc films to iodine and bromine resulted in ordered film structures different from the pure phthalocyanines.

Iodine apparently bonded strongly to the copper substrate displacing the phthalocyanine molecule, which remains in the film, to a likely edge-bonded position. The iodine remained after the phthalocyanine was thermally desorbed at a temperature lower than was usually required to sublime the phthalocyanine from the surface. This is likely due to the weakening of the Van der Waals bonding of the Pc to the copper due to the upright orientation of the molecule.

Unlike iodine, bromine does not appear to bond so strongly to the copper, compared to the phthalocyanine, that it dominates the structure. The large surface unit mesh is compatible with a structure with the phthalocyanine essentially parallel to the copper. LEED measurements are not able to locate the phthalocyanine or bromine molecules in this cell however so there may be several phthalocyanines in the cell in complex configurations. The thermal desorption of the phthalocyanine leaving a bromine pattern indicates that the phthalocyanine bonding to the copper is also weakened in this case from the configuration parallel to the copper seen for pure phthalocyanine.

5.2 Current Injection Pumping

We did not observe any fluorescence on current injection pumping of the metal/phthalocyanine/metal devices that were constructed. Conduction through the devices showed space-charge-limited behavior typical for organic semiconductors. This result was not surprising since these devices did not have phthalocyanine films with epitaxial structure

because of the film thickness limit we encountered for maintaining a stacked ring structure. The devices studied had amorphous or polycrystalline film structures and were thus no different from previously studied devices dominated by molecular properties.

In the pure molecular crystal, carrier transport is generally considered as a hopping process involving localized excitations^[31]. Conductivity in the stacked ring or cofacially joined phthalocyanines often appears metallic or band-like down the organic ligand rings^[32]. If layered structures of undoped materials are grown this would result in confinement of excitons to two dimensional layers. Because of change in central metal atoms between layers, energy differences between different metal- phthalocyanines will create an exciton well. Failure to keep a stacked ring film structure limits carrier transport to local excitations not allowing creation of an exciton well.

6 Recommendations

The ability to grow ordered stacked ring structures of phthalocyanine is crucial to the control of the electronic structure modulation of a film that would lead to charge carrier confinement and resulting optical emission. The weak interaction between the layers of phthalocyanine molecules is not sufficient to produce crystal structures initiated and controlled by the substrate interaction for films thicker than about 5nm. The layers of the film need to exhibit more directional bonding than the Van der Waals bonding of the molecular crystal to allow registry for thicker films. We did not see such bonding, typical of cofacially joined materials^[33] such as SiPcO, using the gas phase molecular doping of this study. A possible approach not well explored in this Phase I study would be ion assisted deposition in an oxygen atmosphere to introduce bonding between the layers.

Once ordered films of phthalocyanine can be grown to any thickness by molecular beam epitaxy the rapid developments in the area of novel electrical and spectroscopic properties of partially reduced and oxidized stacked ring phthalocyanine materials^[34] promise many possible approaches to developing these materials as thin film emitters.

Dopant materials with different oxidation and reduction strengths introduced from the gas phase during film growth should be explored. Our previous work showed dopants such as bromine and dibromomethane had an effect on the emission spectrum.

References

1. E.I. Alshits, R.I. Personov, A.M. Pyndyk and V.I. Stogov, "Dependence of the fluorescence spectra of organic molecules in solid solution on the wavelength of laser excitation", *Opt. Spectrosc.*, **39**, 156 (1975).
2. P.P. Sorokin and J.R. Lankard, *IBM Journal*, **162**, March 1966.
3. M. Romagnoli, M.D. Levenson and G.C. Bjorklund, "Frequency-modulation polarization spectroscopy detection of persistent spectral holes", *J.Opt.Soc.Am. B: Opt.Phys.*, **1**, 571, 1984.
4. D. Eastwood, L. Edwards, M. Gouterman and J. Steinfeld, "Spectra of Porphyrins Part VII. Vapor Absorption and Emission of Phthalocyanines", *J.Molecular Spectroscopy*, **20**, 381 (1966).
5. Katsumi Yoshino, Masakazu Hikida, Kyoichi Tatsuno, Keiichi Kaneto and Yoshio Inuishi, "Emission Spectra of Phthalocyanine Crystals", *J.Phys.Soc. Japan*, **34**, 441 (1973).
6. L. LeMoigne, R. Even, "Spectroscopic Properties and conductivity of thin films of partially reduced metallo-phthalocyanines", *J.Chem. Phys.* [83], 6472 (1985); J. LeMoigne and R. Even, "Spectroscopic Properties and conductivity of thin films of partially reduced metallo-phthalocyanines", *J.Chem. Phys.*, **83**, 6472 (1985).
7. Brian Hoffman and J.A. Ibers, "Porphyrinic molecular metals", *Acct.Chem.Res.*, **16**, 15, 1983; C.J. Schramm, D.R. Stojakovic, B.M. Hoffman, and T.J. Marks, *Science* **200**, 47, 1978.
8. C.W. Dirk and T.J. Marks, "Cofacial assembly of partially oxidized metallomacromolecules as an approach to controlling lattice architecture in low dimensional molecular solids", *Inorg.Chem.* **23**, 4325, 1984.)
9. T.Inabe, T.J. Marks, R.L. Burton, J.W. Lyding, W.J. McCarthy, C.R. Kannewurf, G.M. Reising and F.H. Herstein, "Highly conductive metallophthalocyanine assemblies. Structure, charge transport, and anisotropy in the metal-free molecular metal $H_2(Pc)I$ ", *Solid State Commun.* **54**, 501-4, 1985.
10. J. Martinsen, S.M. Palmer, J. Tanaka, R.C. Greene and Brian Hoffman, "Nickel phthalocyanine iodide: a highly one dimensional low temperature molecular metal", *Phys.Rev. B.* **30**, 6269, 1984.
11. T.W. Barrett, "Modulation of the Electrical Conductance of Phthalocyanine Films by Circularly Polarized Light", *Thin Solid Films.* **102**, 231, 1983.
12. L. LeMoigne, R. Even, "Spectroscopic Properties and Conductivity of Thin Films of Partially Reduced Metallo-Phthalocyanines", *J. Chem. Phys.* **83**, 6472, 1985.
13. J.C. Buchholz and G.A. Somorjai, "The surface structure of phthalocyanine monolayers and vapor grown films: A low energy electron diffraction study", *J.Chem.Phys.* **66**, 573, 1977.
14. Brian Hoffman and J.A. Ibers, "Porphyrinic molecular metals", *Acct.Chem.Res.*, **16**, 15, 1983; C.J. Schramm, D.R. Stojakovic, B.M. Hoffman, and T.J. Marks, *Science* **200**, 47, 1978.
15. T. Kobayashi, K. Yase and N. Uyeda, *Acta Crystall. B. Struct.Sci.* **B40**, 263, 1984; Y. Saito and M. Shiojiri, *J.Cryst.Growth*, **67**, 91, 1984; N. Uyeda, T. Kobayashi and E. Suito, *J.Appl.Phys.*, **43**, 5181, 1972; M. Ashida, *Bull.Chem.Soc.Japan*, **39**, 2625, 1966; Y. Saito, "Epitaxial growth mechanism of chlorinated copper phthalocyanine on KCl surfaces", *Appl. Surf. Sci.* **22-23**, pt.2, 574-81, 1985.
16. T. Permien, R. Engelhardt, C.A. Feldmann and E.E. Koch, "Angle resolved photoemission from oriented films of lead phthalocyanine on a copper (100) surface", *Chem.Phys.Lett.* **98**, 527, 1983.
17. E.I. Alshits, R.I. Personov, A.M. Pyndyk and V.I. Stogov, "Dependence of the fluorescence spectra of organic molecules in solid solution on the wavelength of laser excitation", *Opt. Spectrosc.*, **39**, 156 (1975).
18. D. Eastwood, L. Edwards, M. Gouterman and J. Steinfeld, "Spectra of Porphyrins Part VII. Vapor Absorption and Emission of Phthalocyanines", *J.Molecular Spectroscopy*, **20**, 381 (1966).

19. R.I Personov, E.I. Al'shitz, L.A. Bykovskaya and B.M. Kharlamov, Soviet Phys.JETP, 38 912 (1974).
20. D. Eastwood, L. Edwards, M. Gouterman and J. Steinfeld, "Spectra of Porphyrins Part VII. Vapor Absorption and Emission of Phthalocyanines", J.Molecular Spectroscopy, 20, 381 (1966).
21. Katsumi Yoshino, Masakazu Hikida, Kyoichi Tatsuno, Keiichi Kaneto and Yoshio Inuishi, "Emission Spectra of Phthalocyanine Crystals", J.Phys.Soc. Japan, 34, 441 (1973).
22. Katsumi Yoshino, Masakazu Hikida, Kyoichi Tatsuno, Keiichi Kaneto and Yoshio Inuishi, "Emission Spectra of Phthalocyanine Crystals", J.Phys.Soc. Japan, 34, 441 (1973).
23. E.I. Kapinus, V.P. Staryi, I.I. Dilung, "Influence of nature of central metal atom in tetrapyrrole pigments on triplet state deactivation processes", Theor. And Exp. Chem. (USA) [21],1, 58-62 (1985).
24. Katsumi Yoshino, Masakazu Hikida, Kyoichi Tatsuno, Keiichi Kaneto and Yoshio Inuishi, "Emission Spectra of Phthalocyanine Crystals", J.Phys.Soc. Japan, 34, 441 (1973).
25. S. Muralidharan, G. Ferraudi and L.K. Patterson, "Luminescence from Upper Electronic Excited States of Phthalocyanines", Inorganica Chimica Act., 65, L235 (1982).
26. H.C. Wolf, "Excited State Interaction and Energy Transfer Between Molecules in Organic Crystals- Basic Experimental Methods and Results", p.2 in Organic Molecular Aggregates , eds. P.Reineker, H.Haken, and H.C.Wolf, Solid-State Sciences Series 49, (Springer-Verlag, Berlin, 1983).
27. 1985 NSF-SBIR Phase I Final Report.
28. A. Sussman, "Space-Charge-Limited Currents in Copper Phthalocyanine Thin Films", J. Of Applied Physics. 38, 2738, 1967.
29. A. Sussman, "Space-Charge-Limited Currents in Copper Phthalocyanines Thin Films", J. Of Applied Physics. 38, 2738, 1967.
30. R. D. Gould, "D. C. Electrical Measurements on Evaporated Thin Films of Copper Phthalocyanine", Electronics and Optics. 125, 63, 1985.
31. C.B. Duke, "The localization of injected charges in polymers and molecular solids", Can. J. Chem., 63, 236-42, 1985; C.B. Duke, "Electronic Excitations in Molecular Solids", p.11 in Organic Molecular Aggregates , eds. P.Reineker, H.Haken, and H.C.Wolf, Solid-State Sciences Series 49, (Springer-Verlag, Berlin, 1983).
32. P.D. Hale and M.A. Ratner, "Conductivity mechanisms in phthalocyanine-based 'molecular metals':calculation of the temperature-dependent resistivity", J. Chem. Phys. 83, 5277 (1985).
33. T.Inabe, M.K. Moguel, T.J. Marks, R. Burton, J.W. Lyding and C.R. Kannewurf, "Electronic properties of the conductive polymers SiPcO with different doping agents", Mol.Cryst.Liq.Cryst. 118, 349, 1985.
34. L. LeMoigne, R. Even, "Spectroscopic Properties and conductivity of thin films of partially reduced metallo-phthalocyanines", J.Chem. Phys. [83],6472 (1985); J. LeMoigne and R. Even, "Spectroscopic Properties and conductivity of thin films of partially reduced metallo-phthalocyanines", J.Chem. Phys., 83, 6472 (1985).